Methyl Acrylate by Pyrolysis of Methyl Acetoxypropionate

EFFECT OF PRESSURES OF 1 TO 67 ATMOSPHERES

Methyl acrylate was made by pyrolyzing the acetyl derivative of methyl lactate in stainless steel equipment at various temperatures and pressures between 500° and 625° C. and 1 to 67 atmospheres. Moderate pressures had little effect, but lower yields of methyl acrylate were obtained at the higher pressures, primarily because of the formation of the dimer and higher polymers of methyl acrylate. Other by-products were formaldehyde, acetaldehyde, methyl acetate, carbonaceous material, oxides of carbon, and gaseous hydrocarbons. High yields of methyl acrylate and acetic acid were obtained below 565° C. under approximately atmospheric pressure. The decomposition of the ester appears to be a reaction of the first order. Specific velocity constant (sec.$^{-1}$) is illustrated by the equation:

$$K_1 = 7.8 \times 10^9 \times e^{\frac{-38{,}200}{RT}}$$

THE pyrogenic transformation of a lactic acid derivative (*4, 17, 18, 19*), methyl α-acetoxypropionate, into methyl acrylate (Equation 1) has been studied extensively both because of the low cost of carbohydrates, from which lactic acid is made by fermentation, and because of the growing importance of methyl acrylate as a resin (*13*) and synthetic rubber intermediate (*2, 6, 7, 20, 22*). Recent improvements in the preparation of methyl lactate and methyl α-acetoxypropionate (*8, 9, 10*) from lactic acid and in the preparation of higher acrylates from methyl acrylate (*15*) have lent added interest to the process.

$$CH_3COOCH(CH_3)COOCH_3 \xrightarrow{550^\circ\ C.} CH_3COOH + CH_2{:}CHCOOCH_3 \quad (1)$$

Previous papers (*11, 19*) described the effects of temperature, contact time, and contact materials on the thermal decomposition represented by Equation 1. This paper presents results obtained in a study of the pyrolysis of methyl acetoxypropionate in stainless steel equipment at pressures from atmospheric to 1000 pounds per square inch (66.7 atmospheres). The scale of operation was considerably larger than any hitherto reported for this pyrolysis.

Possibly the most conspicuous advantage of high pressure is hat it increases the throughput of a given pyrolysis unit. Throughput at 67 atmospheres, for example, is 67 times that obtained at 1 atmosphere. In addition, if the reaction is kinetically of order higher than one, increased pressure would be expected to increase the reaction rate more than proportionally. Heat transfer is also more efficient at increased pressures.

On the other hand, increased pressure may have some deleterious effects. It expedites side reactions if they are kinetically of a higher order than one. High pressure also raises the boiling points of reagent and products, and hence these exist in the liquid phase at higher temperatures, making it easier for liquid-phase side reactions to occur. Such liquid-phase reactions might be (*a*) formation of methyl acetate by ester interchange, (*b*) production of acrylic acid, acetoxypropionic acid, and methyl acetate by acidolysis, and (*c*) polymerization of methyl acrylate. One other conceivable effect is the reversal of the desired reaction, according to the principle of Le Chatelier (*16*). It was estimated by the method of Bruins and Czarnecki (*3*) that the magnitude of this effect might be appreciable, but the applicability of this method can be questioned because the thermal decomposition is not necessarily reversible; methyl β-acetoxypropionate might be formed instead of the alpha isomer.

PREPARATION AND PROPERTIES OF METHYL ACETOXYPROPIONATE

The reagent was prepared from methyl lactate and acetic anhydride (*5, 8*), and that used in most of the experiments was redistilled through efficient columns. When the methyl acetoxy-

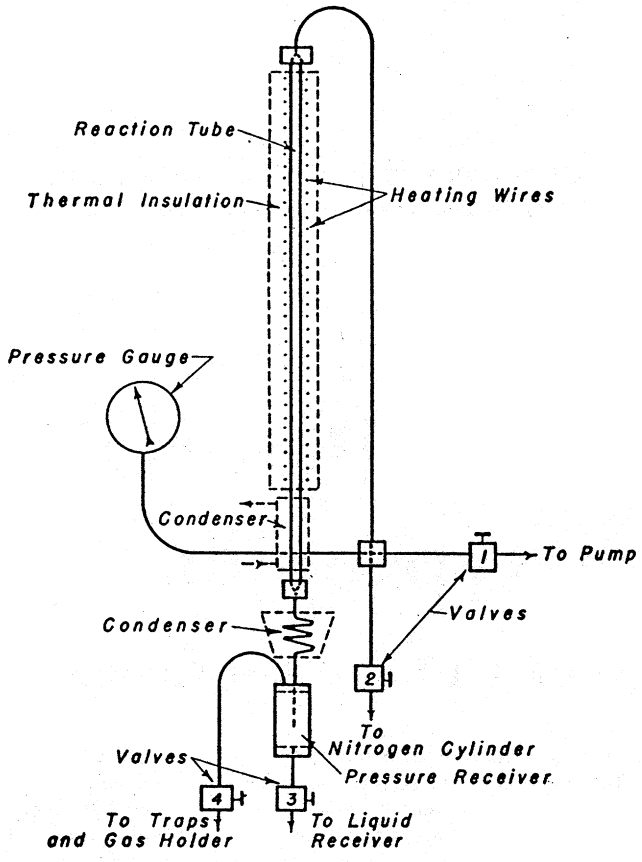

Figure 1. Diagram of *EL* Pyrolysis Apparatus

propionate was not carefully redistilled prior to pyrolysis, no appreciably different results were observed.

One large sample was carefully distilled through a column packed with stainless steel rings (*21*), and the specific gravities and refractive indices of several middle fractions were determined at various temperatures. The refractive index was measured by an Abbe refractometer and the specific gravities by a hydrometer 25 cm. long. Values for these physical constants were plotted against temperature, and a smooth curve was drawn among the points. Values from this curve are presented in the following table. The molecular refraction calculated from the physical constants determined at 20° C. was 33.26 (theoretical, 33.22).

Temp., ° C.	Refractive Index	Specific Gravity Determined	Specific Gravity From literature (*14*)
17	1.4110	1.0907	1.091
20	1.4095	1.0875	1.088
25	1.4070	1.0823	1.082
30	1.4045	1.0770	1.076

PYROLYSIS

EQUIPMENT. The earlier experiments, designated by the prefix *BM*, were carried out in equipment of the Central Experiment Station of the U. S. Bureau of Mines at Pittsburgh. The pyrolysis equipment at this laboratory, employed for the later *EL* experiments, was generally similar to that used at the Bureau of Mines. The reaction tube was a 4.3-meter length of 18-8 stainless steel tubing, having a diameter of 14 mm. outside and 8 mm. inside, heated electrically over a length of 3.5 meters. It was insulated with asbestos pipe covering 2 inches thick.

Four heating sections were used; one (covering 40 cm. of the tube) served as a preheater, and the other three (each covering 105 cm.) served as main heaters. The temperature of each heating section was independently controlled; for this purpose two millivoltmeter-type controllers and a two-point recording and controlling potentiometer were used.

Nine chromel-alumel thermocouples were employed. They were spaced with one at the center of each heating section, one at each of the junctions of the heating sections, and one at each end of the heated zone. They were attached by silver solder to the outside of the tube wall. The leads were brought to a selector switch connected to a potentiometer. In a typical run the temperature of any control couple did not vary more than 10° C. from its average value. At certain points along the tube, however, the average temperature deviated as much as 50° C. from the average of the control couples. The control average for the three main heaters is reported in the tables as the pyrolysis temperature.

The connecting pressure tubing of the *EL* system was 18-8 stainless steel having a diameter of 6 mm. outside and 3 mm. inside. The pressure receiver, which was a modified hydrogenation bomb, and the valves and fittings were cold-rolled steel. Joints were made by the high-pressure closure technique of the American Instrument Company (*1*).

The *EL* pyrolysis tube was mounted vertically, and the reagent was pumped to the top of the pyrolysis tube, whence it flowed downward. At the bottom of the reactor the condensers were installed; these included a water jacket at the lower end of the reactor and a coil of smaller-diameter tubing immersed in a vessel filled with water.

The reagent was delivered by the pump through valve 1 (Figure 1) to the cross, whence it traveled to the top of the reactor at the pressure shown by the gage. Before starting an experiment, nitrogen gas was admitted from a tank through valve until the reaction pressure was reached.

The products were condensed at the lower end of the reactor and traveled to the bottom of the receiver through a drip tube. The liquid products were released intermittently through valve 3 and the overhead gases through valve 4, which was connected to a wet test meter and gas holder through two traps cooled with solid carbon dioxide.

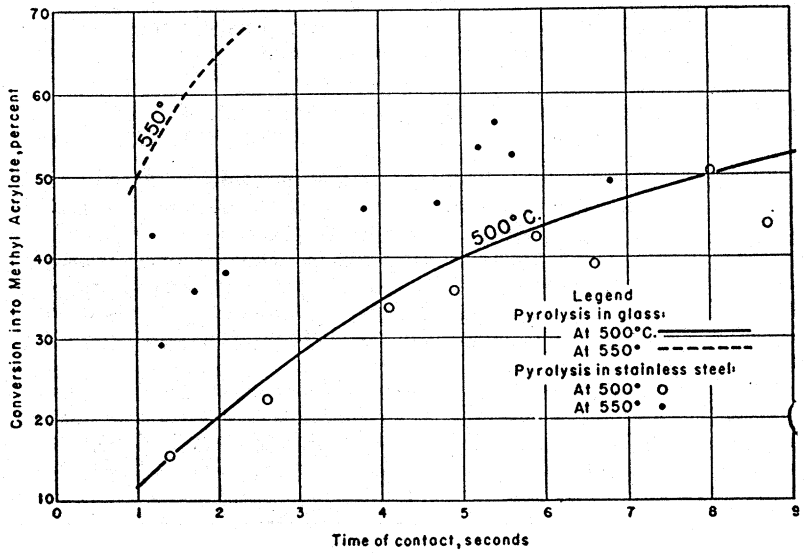

Figure 2. Relation between Conversion into Methyl Acrylate and Time of Contact

TABLE I. PYROLYSIS OF METHYL ACETOXYPROPIONATE AT ATMOSPHERIC PRESSURE

Expt. No.	Av. Temp., ° C.	Contact Time, Sec.	Total Grams Pyrolyzed	Liquid Products, % of Charge	Methyl Acetoxypropionate Decomposed, %	Conversion, % To methyl acrylate	Conversion, % To acetic acid	Yields, % of Theoretical[a] Methyl acrylate	Yields, % of Theoretical[a] Acetic acid
				First Series					
*EL*1	498	8.7	219	90[b]	55.4	42.6	45.2	76.8	81.7
*EL*2	494	6.6	376.0	95.3	42.1	34.8	36.5	83.0	86.8
*EL*3	494	8.0	390.0	98.5	48.8	46.0	50.4	94.8	104.6
*EL*4	499	5.9	608.0	99.4	46.1	41.8	47.0	90.6	102.0
*EL*5	497	4.1	963.7	97.2	38.0	31.5	35.4	83.0	93.5
*EL*6	500	4.9	803.0	100.3	39.5	35.7	40.9	89.9	104.0
*EL*7	501	2.6	828.8	98.6	26.9	22.7	25.9	84.6	98.4
*EL*8	497	1.4	1626.7	99.0	15.2	13.5	14.3	88.4	95.7
*BM*2[c]	546	20.4	194	90.0	90.2	74.5	84.5	80.8	91.6
*EL*9	548	1.3	1624.8	99.7	30.7	27.9	31.4	90.8	103.2
*EL*10	548	1.7	1610	100.0	39.2	34.4	38.8	87.8	98.2
*EL*11	553	2.1	1590	100.5	44.2	40.1	45.9	90.9	104.3
*EL*12	555	3.8	1065	99.5	55.3	49.6	57.7	89.7	104.5
*EL*13	552	4.7	1090	97.2	57.1	48.1	55.1	84.2	97.1
*EL*14	550	5.6	910	96.8	61.0	52.4	59.2	86.0	97.8
*EL*15	550	5.2	660	93.5	66.2	53.3	63.8	80.5	96.3
				Second Series					
*EL*27	600	4.7	590	96.7	87.2	69.6	90.1	79.8	104.2
*EL*28	629	4.1	606.1	84.2	69.2	40.8	64.5	59.0	92.6
*EL*29[d]	625	4.1	506.6	76.1	66.5	39.4	36.0	59.3	54.8
*EL*32[d]	598	1.1	1851	91.2	63.1	48.3	54.7	76.6	87.8
*EL*33	551	1.2	1778	97.4	50.0	43.9	47.4	87.9	96.5
*EL*34	566	1.1	1968	97.1	65.8	56.1	62.9	85.4	97.3
*EL*35	602	2.0	595.1	87.5	64.0	47.2	48.7	73.2	77.2
*EL*36	576	2.8	1043	87.4	92.8	74.1	78.6	80.8	85.8
*EL*37[d]	574	2.8	974	88.2	86.1	66.7	73.5	77.6	86.0
*EL*38[e]	628	2.2	766	84.3	78.6	51.0	64.7	64.3	83.3
*EL*39[d]	552	6.8	510.6	81.5	81.0	51.2	64.9	63.3	81.1
*EL*40[d]	554	5.4	415.5	94.5	75.1	60.4	67.5	80.3	91.0
*EL*41	565	1.0	1439	97.6	59.4	48.9	56.0	82.6	97.1

[a] On basis of starting material not recovered.
[b] Estimated.
[c] Conducted at 5 pounds per square inch gage pressure.
[d] Before this run, the tube was cleaned with water vapor at high temperature.
[e] The reagent contained 1.94% distilled water.

Reagent was delivered to the pump from a buret assembly consisting of two one-liter burets connected to a two-way stopcock. The latter was sealed to a 10/30 ground-glass joint, which fitted in a joint ground into a length of copper tubing attached to the pump.

A Milton Roy pump (type MD-1, with $^5/_{16}$-inch piston, rated at 1.5 gallons per hour maximum at a discharge pressure of 1500 pounds per square inch) was used in some of the experiments. The pumping chamber, valves, and pistons were of 18-8 stainless steel. The pump used in other experiments was a Wilson chemical pump (DES-1 diaphragm type) with a stainless-steel pumping chamber.

PROCEDURE. In most of the experiments, products resulting from pyrolysis of all the material pumped were collected and analyzed. In the experiments carried out at high pumping rates, however, (*BM*9 to *BM*19, inclusive, and *EL*26, *EL*18A to *EL*23) the pyrolysis was conducted for 30 minutes to bring the system to a steady state; products collected within this time were discarded, and products collected under steady conditions were analyzed. The rate of feeding was checked by the buret calibrations. In all the *BM* experiments the amount of reagent fed was computed from the volume of reagent delivered. In the *EL* experiments the reagent was weighed into the buret, and feeding was discontinued when the level of the reagent reached a fixed mark, which indicated removal of a definite weight.

On the assumption that there was no change in volume, the contact time for all the runs was computed by the formula

$$TC = 43.9 \times \frac{V_e}{N \times T} \times P$$

where TC = time of contact
V_e = converter volume, in cc., within 15° of reaction temperature
N = moles of reagent pumped per hour
T = absolute temperature
P = pressure, atmospheres

ANALYSES OF PRODUCTS

Distillation through a Weston column (usually with 25-gram samples) or a column (30.5 cm. long and 1 cm. in diameter) packed with small copper helices (*21*) was used as one analytical method. Since the column packed with copper helices gave better fractionation, products of most of the *BM* experiments and of all of the *EL* experiments were distilled with this apparatus, 75-gram samples being used. The fractions obtained up to 75°, 75° to 100°, 100° to 140°, and 140° to 200° C. were collected and weighed. Distillation curves were plotted and used to estimate both the nature and amounts of distillate boiling in the pyrolyses. In runs characterized by appreciable amounts of distillate boiling below 75° C., yields were computed by considering the fraction collected between 75° and 100° C. as methyl acrylate. In other runs, all the material collected below 100° C. was considered methyl acrylate. The material distilling below 75° C. contained considerable acrylate.

Distillations were conducted by two operators, and the two analyses usually agreed within 3%. Distillation of mixtures of pure methyl acrylate, acetic acid, and methyl acetoxypropionate showed that a skilled operator using the copper-packed still could recover 98% of each component charged to the still.

In addition to being subjected to distillation analysis, the products were analyzed for acid by titrating aliquots with standard alkali; the acid content was computed as acetic acid.

In the examination of products from experiment *EL*26 and later ones, the distillation analyses were supplemented by saponification and titration of the distillate fractions. In almost every case the amounts of both esters as determined by this method were lower than those determined by distillation. Nevertheless, results by the two methods usually agreed within 4%. The values reported in the tables are averages of the various determinations.

PYROLYSIS AT ATMOSPHERIC PRESSURE

The runs were made in two series, one preceding, the other following, the *EL* high-pressure runs. The data are summarized in Table I. The relation between contact time and conversion into methyl acrylate is shown by the positions of the dots and circles in Figure 2. For comparison, Figure 2 includes curves based on the same contact times from the literature (*19*). The original curve was plotted on the basis of 30 cc. of packing material in a glass tube, and since the volume within 15° of reaction temperature in the glass tube was also approximately 30 cc., no correction was necessary.

Data in Figure 2 were corrected to 500° and 550° C. with the aid of data from the literature (*19*). It is apparent that at 500° C. the conversion in the stainless steel equipment was almost the same as in the glass tube. However, it appears that at 550° C. the reaction went much more slowly in the steel tube; furthermore, reproducibility was not especially good. With contact times of 1.3 and 1.2 seconds, one experiment (*EL*9, Table I) differed from another (*EL*33, Table I) by about 16% in the conversion to methyl acrylate. The fact that these results occurred in different series may partly explain this discrepancy, as will appear later.

Table I indicates that the yields of methyl acrylate in most of the runs at 500° and 550° C. were satisfactory. The yields are based on the methyl acetoxypropionate not recovered, and hence any mechanical, distillation, and other losses would result in

TABLE II. PYROLYSIS OF METHYL ACETOXYPROPIONATE AT INCREASED PRESSURES

Expt. No.	Av. Temp., ° C.	Gage Pressure, Lb./ Sq. In.	Contact Time, Sec.	Grams Pyrolyzed	Liquid Products, % of Charge	Methyl Acetoxypropionate Decomposed, %	% Conversion to: Methyl acrylate	% Conversion to: Acetic acid	Yields, % of Theoretical[a] Methyl acrylate	Yields, % of Theoretical[a] Acetic acid
				Experiments at About 550° C.						
*BM*3	540	45	20.4	196.5	87.5	100	63.1	92.2	63.1[b]	92.2
*BM*4	547	45	27.0	231.6	81.4	100	57.4	92.2	57.4[b]	92.2
*BM*5	550	45	20.8	315.5	85.4	100	65.6	98.9	65.6[b]	98.9
*BM*6	544	45	9.2	532.8	92.6	100	76.2	98.3	76.2[b]	98.3
*BM*7	547	45	4.5	1060	95.5	91.2	72.7	94.2	79.7[b]	103.1
*EL*24	547	50	3.3	2150	93.2	70.0	55.8	66.9	79.7[b]	96.3
*EL*25	547	100	3.1	3590	96.4	68.6	58.4	67.3	85.2[b]	98.4
*BM*8	544	135	26.8	616	78.5	100	45.7	92.6	45.7	92.6
*BM*9	547	135	14.6	858	88.9	100	61.1	100.0	61.1	100.0
*EL*26	547	150	2.9	4760	95.0	70.9	54.0	68.3	76.1	96.0
*EL*23	549	300	4.2	4850	96.0	81.9	63.7	82.7	77.7	100.8
*EL*22A	547	500	7.1	6470	89.5	93.1	54.6	90.9	58.6	94.8
				Experiments at 500° C.						
*EL*16	498	50	3.9	2120	96.7	33.2	27.1	31.6	79.7	94.3
*EL*17	498	100	3.9	4370	99.3	34.9	26.2	31.9	75.8	93.3
*BM*14	502	135	14.3	1110	92.8	79.6	56.5	76.5	72.0	96.3
*BM*15	498	135	31.1	502	93.1	93.4	60.8	96.6	65.2	103.4
*BM*16	500	360	16.4	1318	91.7	80.9	52.4	72.3	64.8	90.6
*BM*17	493	735	18.5	4675	91.6	84.4	48.4	72.2	56.7	85.9
*BM*18A	488	900	12.3	1580	98.5	42.9	27.8	36.5	66.1	88.7
*BM*19	497	1000	22.5	3725	100.5	87.5	56.2	75.8	64.3	86.5
				Experiments at 450° C.						
*BM*10	448	45	26	168	100.5	93.1	34.4	40.4	86.6	101.5
*BM*11	450	135	65	298	95.3	73.3	52.4	71.7	71.4	97.8
*BM*12	449	135	27	521	98.9	43.4	27.7	45.9	63.9	106.0
*BM*13	452	360	28	1560	100	45.4	28.9	49.2	61.7	107.5

[a] On basis of starting material not recovered.
[b] All distillate collected below 100° C. was considered methyl acrylate.

lowered yields. On a plant scale the yields could probably be increased.

To ascertain whether complete conversion could be obtained in one pass, experiments in the second series were conducted at higher temperatures. Table I shows that higher temperatures did not cause complete conversion and that the results depended largely on the previous use and treatment of the pyrolysis tube. In experiment *EL*27, for example, the yield of methyl acrylate was about normal; yet in certain later experiments (*EL*32 and 35) yields, as well as conversions, were lower in spite of the shorter contact times. Destruction of acetic acid increased in some of the later runs even with short contact times. Table I shows that high temperatures drastically reduced the yields of both methyl acrylate and acetic acid. At 625° C. the yields were poor for both. Even 550° gave reduced yields if the contact time was long (experiment *EL*39). That a similar run in the first series (*EL*14, Table I) gave good yields is further evidence that the history of the tube is important. On the basis of the data in Table I, it appears that 565° C. is about the highest temperature at which good yields can be obtained in the equipment used. This tentative conclusion was made on the assumption that aging would not improve the behavior of the tube.

In the runs characterized by low acrylate yields, the recovery of liquid products was low, and large quantities of gas were formed. Gas formation was invariably accompanied by formation of coke in small hard particles that occasionally choked the outlet of the pyrolysis tube. A hard film of coke was also formed on the tube wall. This was removed by scraping the tube with a stiff wire, by pumping steam through the tube at 500° or drilling from the outlet end with a small cutter head at the end of a flexible shaft. The runs preceded by such cleansing are indicated in Table I by [d]. An initially clean tube, however, was not always satisfactory, as shown by runs *EL*29, *EL*32, and *EL*39. In fact, if there was any difference, a coated tube was better than a clean one. The methyl acrylate yield in run *EL*33 was satisfactory, although it followed a run marked by a low acrylate yield.

In view of the behavior of stainless steel at high temperatures, it seems probable that the lack of reproducibility at 550° and 1.2 seconds was due largely to a change in the condition of the tube wall.

The similarity in behavior of stainless steel at high temperatures to that of iron at lower temperatures (*11*) suggested the use of water to inhibit side reactions. Accordingly, run *EL*38 was carried out at 628° C. with a reagent containing 1.94% distilled water. The yield was still unsatisfactory, but the fact that it was possible to operate at all was evidence that the water inhibited carbonization, for after *EL*29, two attempts were made to operate at 625° C. and each time the pyrolysis tube blocked up within a few minutes. Inhibition of the desired reaction by water (*11*) was not observed here.

Summarizing, the stainless steel equipment was satisfactory for preparing methyl acrylate at 500° C. At 550° C. the reaction proceeded more slowly in stainless steel than in glass, but yields were still satisfactory. Above 565° C. yields decreased because of carbonization. At 550° C., with long contact times, carbonization occurred in some experiments.

PYROLYSIS AT INCREASED PRESSURES

In general, yields of methyl acrylate obtained at increase pressures were not so high as those at atmospheric pressure (Tables I and II). Yields of acetic acid apparently were little affected by increasing the pressure. The lower yields of acrylate were due mainly to the formation of less volatile substances (distilling above 200° C. and 760 mm.), which were probably dimers, trimers, and higher polymers of methyl acrylate. As mentioned later, one fraction of the distillation residue was tentatively identified as methyl acrylate dimer; polymethyl acrylate was also isolated.

The amount of less volatile substances in the pyrolysis product appeared to be mainly dependent on the pyrolysis pressure

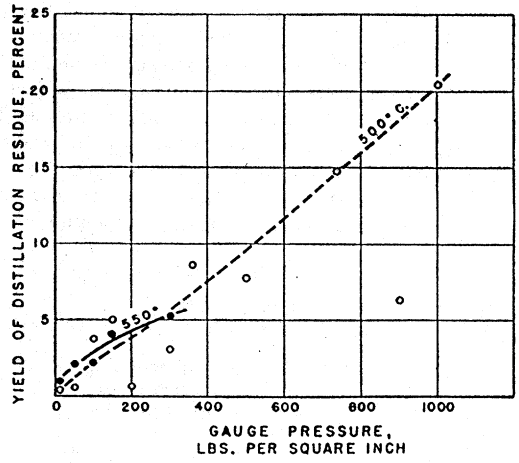

Figure 3. Relation between Yield of Distillation Residue and Pyrolysis Pressure

(Figure 3). While the points in Figure 3 are rather widely scattered, the trend is unmistakable.

Several times, especially at higher pressures, the pyrolysis tubes were entirely blocked by a plug of carbonaceous material. It was usually possible to anticipate coking, for it was preceded by a sudden increase in the rate of gas formation. Formation of residue appeared also to be related to the condition of the tube wall; the run at 900 pounds per square inch, in which there was a relatively small amount of residue (Figure 3), followed a lengthy application of steam to remove a coke plug.

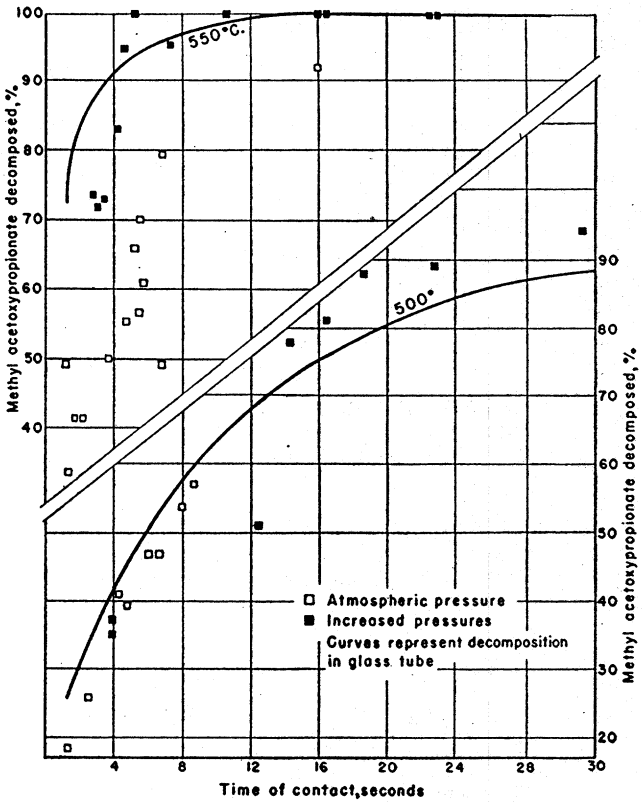

Figure 4. Effect of Contact Time on the Decomposition of Methyl Acetoxypropionate

These facts suggest that carbonization (described in the section on pyrolysis at atmospheric pressure) and the formation of less volatile substances under pressure may be due to the polymerization of methyl acrylate to products of different molecular weights. The lower boiling dimers, trimers, etc., appear as distillation residue; the higher boiling products condense and char, forming gas and coke in the pyrolysis tube. Preparation of dimers and trimers of acrylic esters under pressure has been described (*12*).

Figure 4 shows the conversion of the diester at 500° and 550° C. at both atmospheric and higher pressures. At 500° C. the disparity between data for increased pressure runs, data for atmospheric pressure runs, and previously published data (*19*) for glass tubes was not great; at 550° C. the conversions at atmospheric pressure were considerably less than those obtained at increased pressure and those previously described (*19*) for glass tubes.

Possibly the various effects reported here may be attributed to streamlined flow. Computation based on an assumed viscosity of 0.02 centipoise for the vapors in the tube indicates that the critical Reynolds number would be reached in the increased pressure experiments but not at atmospheric pressure. Hence coke formation at atmospheric pressure might be relatively high because of long contact of some of the vapor at the tube wall.

The effect of turbulence on the pyrolysis at atmospheric pressure is being investigated in a No. 446 steel tube. Preliminary results indicate that with turbulent flow pyrolysis may be carried out satisfactorily above 565° C.

PYROLYSIS BY-PRODUCTS

The large amounts of reaction products processed to recover methyl acrylate and unconverted methyl acetoxypropionate made it possible to investigate some of the by-products formed in the reaction. In the normal runs by-products occurred in minute amounts. In the high-temperature experiments in which carbonization occurred, however, the methyl acrylate fraction did not distill within a narrow temperature range; instead, the distilling temperature increased gradually from about 70° to 80° C. The boiling points of the acetic acid and methyl acetoxypropionate fractions were not affected. The fact that methyl acrylate forms several azeotropes (*15*) made identification of by-products difficult, since the lower boiling material consisted mainly of methyl acrylate. One impurity appeared to be water, collected as the methyl acrylate–water azeotrope. After a number of analytical distillations, a white solid collected in the reflux condenser of the analytical still. When removed, it had a pronounced odor of formaldehyde, an indication that it was probably a formaldehyde polymer. To verify the purity of the methyl acrylate obtained by pyrolysis, the acrylate fractions of two experiments (*EL*32 and *EL*36) were combined and redistilled, and saponification equivalents were determined on two fractions. The first fraction, collected over the range 69–80° C. and amounting to 30% of the charge, had an indicated purity of 94%. The second cut, taken at 80° C., had an indicated purity of 99%.

From the pyrolyses conducted under increased pressure, more by-products were identified; these were found to include both low-boiling and high-boiling substances. Three of the former were identified as acetaldehyde (as the 2,4-dinitrophenylhydrazone derivative), formaldehyde (by its odor), and methyl acetate. (The ester was hydrolyzed; methanol was identified as the 3,5-dinitrobenzoate and α-naphthyl urethan; and acetic acid was identified as the *p*-bromophenacyl derivative.) One high-boiling by-product was tentatively identified as methyl acrylate dimer by its boiling range (113–123° C. at 18 mm.), its saponification equivalent of 86.3, and its unsaturation. In addition, a soft resin, presumably polymethyl acrylate, was isolated from the distillation residues by precipitation with methanol. As mentioned above, gases were formed as reaction by-products. Even under the best conditions, a small amount of gas was formed; this consisted mainly of carbon monoxide, carbon dioxide, and unsaturated hydrocarbons. When gas evolution was pronounced, the gas consisted of carbon monoxide, carbon dioxide, saturated hydrocarbons, and unsaturated hydrocarbons in descending order of quantity.

Rapid cooling of the vapors and condensate leaving the pyrolysis tube probably would decrease the side reactions in the liquid phase.

KINETICS OF THE REACTION

A preliminary investigation of the kinetics of the reaction was made, based on the following assumptions: (1) The methyl acetoxypropionate disappears only via the decomposition into methyl acrylate and acetic acid; (2) the time of contact (reaction time) is equal to the free volume of the reactor divided by the average volume of the vapors entering and leaving per second. The first assumption led to the exclusion of any experiment in which the recovery of liquid products was less than 90%. The contact time was found by multiplying the contact time in the tables by $2/(2 + x)$, where x is the fraction of the diester converted.